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Temperature variation of X-ray Debye temperature of KCl, KBr and KI

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An isobaric Gruneisen parameter which includes the effect of crystal anharmonicity due to isothermal volume expansion and isochoric self-energy effect has been evaluated in the case of alkali halide crystals. Paskin's theory regarding the temperature variation of the X-ray Debye temperature has been modified so as to include the additional anharmonicity due to isochoric anharmonic effect. The calculated results on KCl, KBr and KI show fair agreement with the experimental data.

1. Introduction

The temperature variation of the phonon frequencies of a crystal is due to isothermal and isochoric anharmonic effects. The isothermal Gruneisen parameter (Gruneisen 1926) gives the phonon frequency shift which is due to the isothermal volume changes in the crystal. The isochoric self-energy anharmonic phonon frequency shift has been investigated by various workers (Maradudin & Fein 1962, Cowley & Cowley 1966 and Cowley 1963). An analysis of the experimental results on KCl, KBr and KI (Lowndes 1970) showed that the anharmonic frequency shift due to isochoric self-energy effect is larger than the isothermal shift. Lowndes (1970) has further shown that the frequency shifts calculated in the case of KBr by using pertubation method (Cowley 1963), are not in agreement with his experimental results.

We therefore introduced a thermodynamic method (Tolpadi 1974, 1975a, 1975b) of evaluating the isobaric Gruneisen parameter and it is found that the calculated anharmonic frequency shifts of KBr are in satisfactory agreement with the experimental data of Lowndes (1970). It has been further shown that the isochoric anharmonic correction must be applied in the study of the temperature variation of the X-ray Debye temprature of cubic metals (Tolpadi 1975, 1975c). In the present study we have investigated the temperature variation of the X-ray Debye temperature of alkali halide crystals.

2. Theory

It has already been shown (Tolpadi 1975, 1975a, 1975b) that

$$d\nu = -\nu(\alpha\gamma_v dT + \gamma_T dV/V) \qquad \ldots (1)$$

where $\gamma_v = -(1/\alpha\nu)(\partial\nu/\partial T)_v$ and $\gamma_T = -(V/\nu)(\partial\nu/\partial V)_T$.

In eq. (1) α is the volume expansion coefficient, γ_v is the isochoric Gruneisen parameter and γ_T is the isothermal Gruneisen parameter. The terms $\nu\alpha\gamma_v dT$ and $\nu\gamma_T dV/V$ are the phonon frequency shifts due to isochoric self-energy and isothermal volume expansion effects.

Using eq. (1), the expression for the isobaric Gruneisen parameter is given by

$$\gamma_p = -\frac{V}{\nu}\left(\frac{\partial\nu}{\partial V}\right)_p = -\frac{1}{\alpha\nu}\left(\frac{\partial\nu}{\partial T}\right)_p = \gamma_v+\gamma_T \qquad \ldots\ \ldots(2)$$

The isobaric Gruneisen parameter $-(1/\alpha\nu)(\partial\nu/\partial T)_p$ is calculated by adopting the following method. The frequency determinant of a cubic crystal in the long wavelength limit is solved along the three symmetry directions. Differentiating the frequency expressions the nine expressions for the isobaric Gruneisen parameters are given by

(100) Direction

$$\gamma_1 = \gamma_2 = -\frac{1}{2\alpha Q_1}\left(\frac{\partial Q_1}{\partial T}\right)_p - \frac{1}{6} \qquad (T_1, T_2)$$

$$\gamma_3 = -\frac{1}{2\alpha Q_2}\left(\frac{\partial Q_2}{\partial T}\right)_p - \frac{1}{6} \qquad (L)$$

(110) Direction

$$\gamma_4 = \gamma_1 \qquad (T_1)$$

$$\gamma_5 = \frac{1}{2\alpha Q_3}\left(\frac{\partial Q_3}{\partial T}\right)_p - \frac{1}{6} \qquad (T_2) \qquad \ldots\ (3)$$

$$\gamma_6 = -\frac{1}{2\alpha Q_4}\left(\frac{\partial Q_4}{\partial T}\right)_p - \frac{1}{6} \qquad (L)$$

(111) Direction

$$\gamma_7 = \gamma_8 = -\frac{1}{2\alpha Q_5}\left(\frac{\partial Q_5}{\partial T}\right)_p - \frac{1}{6} \qquad (T_1, T_2)$$

$$\gamma_9 = -\frac{1}{2\alpha Q_6}\left(\frac{\partial Q_6}{\partial T}\right)_p - \frac{1}{6} \qquad (L)$$

where $Q_1 = C_{44}$, $Q_2 = C_{11}$, $Q_3 = (C_{11}-C_{12})$, $Q_4 = (C_{11}+C_{12}+2C_{44})$, $Q_5 = (C_{11}-C_{12}+C_{44})$ and $Q_6 = (C_{11}+2C_{12}+4C_{44})$. In eq. (3) T_1, T_2 and L refer to transverse and longitudinal polarisations.

An average isobaric Gruneisen parameter is obtained by using Houston's formula (Betts *et al* 1956)

$$\gamma_p = (10\gamma_A+16\gamma_B+9\gamma_C)/35 \qquad \ldots\ (4)$$

where $\gamma_A = (\gamma_1+\gamma_2+\gamma_3)/3$. $\gamma_B = (\gamma_4+\gamma_5+\gamma_6)/3$ and $\gamma_C = (\gamma_7+\gamma_8+\gamma_9)/3$. γ_A, γ_B and γ_C are the average Gruneisen parameters along the three symmetry directions (100), (110) and (111) respectively.

Paskin (1957) has shown that the temperature variation of the X-ray Debye temperature θ is given by

$$\frac{\theta(T)}{\theta(0)} = \left\{ \frac{V(T_0)}{V(T)} \right\}^{\gamma_T} \quad \ldots \quad (5)$$

where γ_T is the isothermal Gruneisen parameter. The theory of Paskin considers only the anharmonic effect due to isothermal volume expansion of the crystal.

In a recent study (Tolpadi 1975c) we modified the theory of Paskin so as to include the crystal anharmonicity due to both volume expansion and self-energy effects. The variation of the phonon frequencies when the temperature and volume of the crystal change under constant atmospheric pressure is given by eq. (1). It is assumed that the temperature variation of the Debye frequency of the crystal depends on the average isobaric Gruneisen parameter given in eq. (4). Therefore integrating eq. (1) or (2) we can show that the modified Paskin expression for the temperature variation of Debye temperature is given by

$$\frac{\theta(T)}{\theta(0)} = \left\{ \frac{V(T_0)}{V(T)} \right\}^{\gamma_p} \quad \ldots \quad (6)$$

where γ_p combines the anharmonic effects due to volume expansion and isochoric self-energy effects.

3. Results and Discussion

In the present investigation we have studied the temperature variation of the X-ray Debye temperature in the case of KCl, KBr and KI. The thermal expansion (Richard *et al* 1972) and elastic constant data (Simmons & Wang 1971) have been used to calculate the isobaric Gruneisen parameter from eq. (4). The isothermal Gruneisen parameter is obtained from Gruneisen relation (Gruneisen 1926). Now using eq. (2) an average isochoric Gruneisen parameter can be calculated. The temperature variation of the data on γ_p, γ_T and γ_v is given in table 1 and it is found that the isochoric self-energy effect is less than the isothermal anharmonic effect.

The Debye temperature of KCl, KBr and KI at 300K have been taken as 220K, 160K and 120K respectively (Pathak *et al* 1975). By using eqs. (5) and (6) which refer to the theory of Paskin and the modified theory of Paskin respectively the temperature variation of the Debye temperatures have been calculated and they are given in figure 1. In the case of KI room temperature data on γ_p and γ_T is used to calculate the temperature variation of θ. Pathak and Trivedi (1973)

and Pathak & Pandya (1975) have obtained the experimental data on the temperature variation of the X-ray Debye temperature by adopting Chipman's method (Chipman 1960). These results are also plotted in figure 1. It is found that the calculated results on KI, which are based on the modified theory of Paskin, are in satisfactory agreement with the experimental data of Pathak and Pandya (1975). In the case of KCl and KBr the agreement is not very satisfactory; but it may be noted that the isochoric anharmonic effect also contributes to the temperature variation of the X-ray Debye temperature.

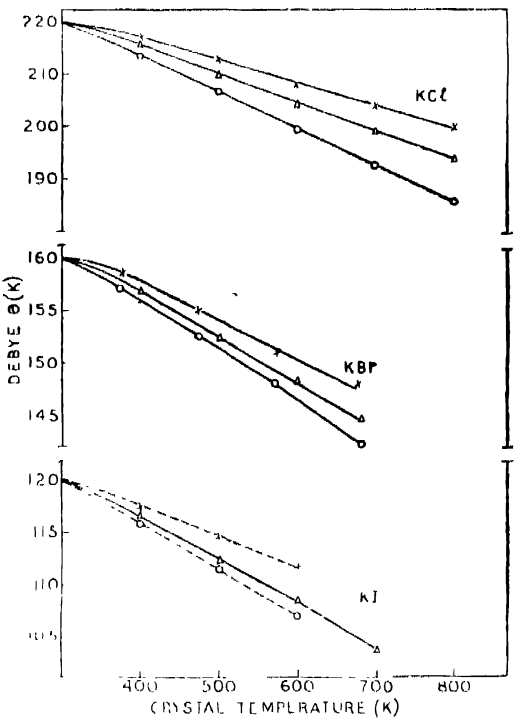

Fig. 1. Temperature variation of X-ray Debye temperature of KCl, KBr and KI. $X-X$ Theory of Paskin, $0-0$ Modified theory of Paskin, $\Delta-\Delta$ Experimental data based on Chipman's method.

Lowndes (1970) investigated the temperature variation of the longwavelength longitudinal optic mode frequencies as determined from Krammers-Kronig analysis of near-normal incidence single crystal reflectance data and from small grazing-angle reflectance data on thin films. By considering the experimental data of Lowndes (1970) the isobaric Grunoisen parameter $\gamma_p = -(1/\alpha\nu)(\partial\nu/\partial T)_p$ is calculated. γ_p is also calculated from eq. (4) by using the relevant data. The X-ray data (Pathak & Trivedi 1973, Pathak & Pandya 1975) on the temperature variation of θ is also used to calculate γ_p and all these results are given in table 2.

The temperature at which γ_p is evaluated is also given in the table. A comparison of the data on γ_p shows fair agreement except in the case of KI.

In the present investigation a modified theory of Paskin is introduced to study the temperature variation of X-ray Debye temperature. It is shown that the crystal anharmonicity due to both volume expansion and the isochoric self-energy effect must be considered in the study of the temperature dependance of the X-ray Debye temperature of alkali halide crystals.

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Table 1. Isobaric, isothermal and isochoric Grueneisen parameters of alkali halide crystals

Crystal	Temperature (K)	Grueneisen parameters γ_p	γ_T	γ_v
KCl	200	2.5	1.44	1.0
	300	2.4	1.45	1.0
	400	2.5	1.46	1.0
	500	2.1	1.48	0.90
	600	2.6	1.49	1.1
	700	2.6	1.50	1.1
KBr	333	2.3	1.47	0.80
	423	2.3	1.49	0.85
	523	2.1	1.51	0.60
	623	2.7	1.50	1.2
	723	3.3	1.49	1.8
	823	2.9	1.47	1.4
KI	200	1.9	1.50	0.4
	270	2.8	1.51	1.3
	290	2.6	1.54	1.1

Table 2. Isobaric Gruneisen parameters as determined from Krammers-Kronig (KK) analysis, from thin-film reflectance data (film) from eq. (4) and from X-ray data

rystal	KK (250K)	Film (250K)	X-ray (400K)	eq. (4) (300K)
KCl	3.2	3.0	2.1	2.5
KBr	2.4	2.4	2.1	2.3
KI	4.5	3.6	2.3	2.8

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